

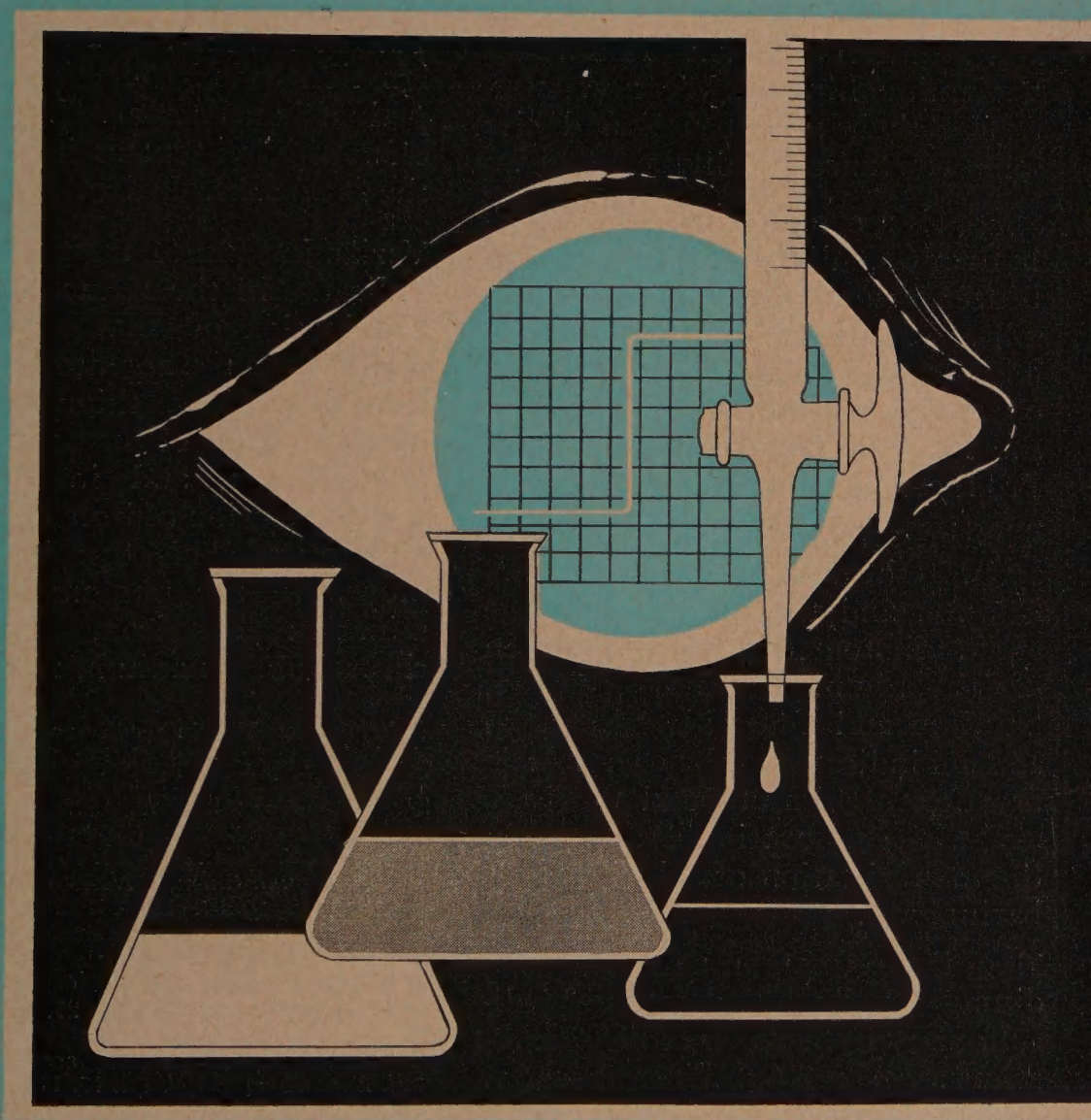
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What's New

Under the J. T. Baker Label



The December issue listed the many items added to the J. T. Baker line during 1958. This group included the chromogenic agents and indicators Thorin, Tiron, and Variamine Blue B. We now summarize their salient uses and cite some references readily available.

Thorin is a common name for 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzenearsonic acid and its sodium salts. (Other common names include Thoron and APANS.) J. T. Baker offers this reagent as item 4125 in the form of the disodium salt. A Product Data Sheet is now available.

Thorin serves as a chromogenic agent in the detection of chromium, lithium, and thorium, and in the spectrophotometric determination of zirconium, thorium, lithium, hafnium, and of fluoride. It serves as a metal indicator in the chelometric titration of bismuth and thorium, and as an adsorption indicator in the microtitration of sulfate with a barium salt.

Tiron is the common name for disodium 1,2-dihydroxybenzene-3,5-disulfonate. J. T. Baker offers this reagent as item 4160. Tiron serves as a chromogenic agent in the photometric determination of titanium, iron, molybdenum, cerium, niobium, and fluoride. In various methods, it acts as a masking agent for iron, aluminum, titanium, chro-

mium, or manganese. Tiron serves as an indicator in the chelometric titration of iron and zirconium.

Variamine Blue B is a common designation for *N*-(*p*-methoxyphenyl)-*p*-phenylenediamine. J. T. Baker offers this reagent as item 4230 in the form of the hydrochloride.

Variamine Blue B serves as a redox indicator in the reductometric determination of iron, cerium, zinc, and lead, in the argentometric titration of halides, thiocyanate, and cyanide, and of potassium tetraphenylboron, and in the chelometric titration of iron, copper, and aluminum. This dye is also employed in the photometric determination of iron, manganese, chromium, vanadium, and silver.

References on Thorin readily accessible include: *Anal. Chem.* 21, 1239 (1949); 24, 1624 (1952); 25, 416, 992, 1219, 1331 (1953); 26, 1593 (1954); 27, 1461 (1955); 28, 812, 1527 (1956); 29, 158 (1957); 30, 1680, 1772 (1958); *Analyst* 77, 154 (1952); *Anal. Chim. Acta* 14, 162 (1956); 19, 458 (1958); *Z. anal. Chem.* 152, 253 (1956); *Am. Ind. Hyg. Assoc. Quart.* 19, 464 (1958); *Chemist-Analyst* 46, 18 (1957). An annotated bibliography on Thorin through early 1957 is available as U.S.A.E.C. Rept. ISC-873, Office Tech. Serv., Dept. of Comm., Washington 25, D. C., 50 cents.

References on Tiron readily accessible include: *Ind. Eng. Chem., Anal. Ed.* 16, 111 (1944); *Anal. Chem.* 19, 100 (1947); 29, 1246 (1957); *Anal. Chim. Acta* 6, 450 (1952); 8, 546 (1953); *Chemist-Analyst* 44, 71 (1955); 46, 46 (1957).

References on Variamine Blue B readily accessible include: *Z. anal. Chem.* 137, 410 (1953); 149, 250 (1956); 153, 401, 411 (1956); 154, 185 (1957); 155, 90 (1957); *Talanta* 1, 377 (1958); *Chemist-Analyst* 46, 76 (1957).

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Spectrophotometric and Photometric Microdetermination of Vanadium

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Vanadium has long been determined colorimetrically by the action of hydrogen peroxide on vanadium(V). Other classical methods are based on the formation of the soluble, yellow phosphotungstovanadate complex, and of the complex formed by vanadium with a mixture of molybdate and phosphate in acidic medium. Further, the absorbance of the vanadyl ion in acidic medium has been measured. Recently, Bermejo Martinez and Prieto Bouza (1) observed that ethylenediaminetetraacetate (EDTA) intensifies the color of vanadyl solutions markedly and permits an improved spectrophotometric and photometric determination of vanadium. From 0.2 to 0.7 milligram of vanadium per milliliter can thereby be determined with very good results by absorption measurements at 558 millimicrons.

A further rapid and simple photometric and spectrophotometric method has now been evolved that has a sensitivity greater or equal to the classical and vanadyl-EDTA approaches mentioned above. The interferences are unusually small in number and are easily resolved; hence, the method is applicable to the determination of microgram amounts of vanadium in complex materials. The method is based on the intense coloration exhibited by acidic solutions of the vanadyl ion on the addition of ethylene glycol bis-(β -aminoethyl ether)-N, N, N', N'-tetraacetic acid (conveniently termed in either the acid or anion form 'EGTA') and hydrogen peroxide.

Preliminary Study. In the development of the final procedure, a study was made of the absorption spectrum at various pH values of a solution of vanadyl ion to which EGTA and H_2O_2 were added. For this study, a sufficient amount of a solution of vanadyl sulfate in H_2SO_4 was taken to correspond to 69 micrograms of vanadium per ml., then 1 ml. of 5% EGTA soln., drops of 2 N NaOH (the acidity of vanadyl soln. is increased by the complex formation), and 1 ml. of 30% H_2O_2 were added, and the volume was made up to 25 ml. with water. Water was used as a blank. It was found that the solution exhibited a characteristic absorption band in the region of 426 millimicrons and the intensity of the absorption did not vary significantly in the pH range 1.52 to 2.42 (as de-

termined by a pH-meter). At lower pH values, EGTA precipitated; at a higher pH, the absorbance decreased rapidly probably due to instability of the complex. At the most favorable pH of 1.70, it is noteworthy that the absorption maximum was shifted slightly toward the visible region. A comparison was made of the absorption spectrum of the vanadyl soln. alone, with H_2O_2 added, and with both EGTA and H_2O_2 added. The comparison which was made at a single vanadium concentration (69 micrograms per ml.) and at pH 1.70, is shown in Figure 1. It will be seen that when EGTA is present the absorption in the visible spectrum is markedly increased.

It was further found that the intensity of the absorption at 426 millimicrons decreased progressively as the concentration of H_2O_2 present was increased. The amount of H_2O_2 employed in the procedure finally developed was found to give satisfactory results and to be sufficient to oxidize all of the vanadium present in the concentration range proposed for the method. It was also established that the presence of a great excess of EGTA was not desirable. (Of course, where foreign ions are present which complex with EGTA, the amount of this reagent must be increased.) In order to obtain optimum results, it was necessary to add the EGTA to the vanadyl soln. *before* the addition of the H_2O_2 .

Reagents. EGTA, 5% soln., made by dissolving the EGTA free acid in sufficient NaOH soln. to form the disodium salt and diluting with water. *Standardized vanadyl soln.*, 0.01 M, prepared by dissolving reagent grade $VOSO_4 \cdot 5H_2O$ in 100 ml. water containing 10 ml. concd. H_2SO_4 , diluting to 1 liter with water, and standardizing by a permanganometric titration. *Other reagents* include 2 N NaOH, 30% H_2O_2 , Clark-Lubs buffer of pH 1.70 (prepared by mixing 13.2 ml. 0.2 N HCl and 25.0 ml. 0.2 N KCl and diluting to 100 ml. with water).

Equipment. In the experimental work, a Beckman DU spectrophotometer and a Spekker absorptiometer, Hilger & Watts, Ltd., Model H-760 with Ilford No. 601 filter, were employed and in each case with 1-cm. Corex cells.

Preparation of Standard Curve. Transfer aliquots of the standardized vanadyl soln. to 25-ml. volumetric flasks, to each add 2 ml. of the EGTA soln., about 10 ml. of buffer, and 1 ml. of 30% H_2O_2 . Adjust the pH to 1.70 (pH-meter) and dilute to mark. Measure the absorbance of these solutions against a water blank. Typical calibration curves for the spectrophotometric and photometric methods are given in Figure 2.

Procedure for Applied Samples. Dissolve the sample by a method appropriate to its composition. Then proceed as given for the preparation of the standard curve substituting an appropriate volume of the sample solution for the standardized vanadyl soln.

Interferences. Very high concentrations of iron (III), titanium(III), copper(II), uranium(VI), molybdenum(VI), and tungsten(VI) interfere and must be removed following initial solution of the

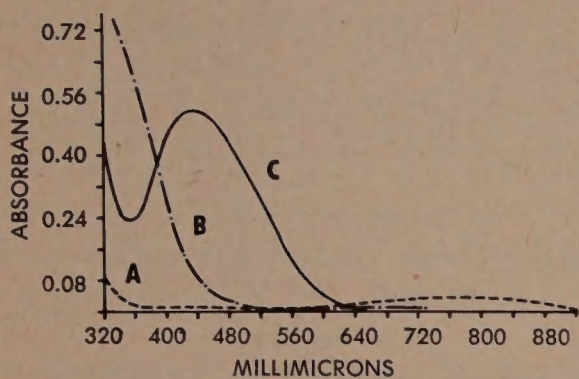


FIGURE 1. ABSORPTION SPECTRUM OF VANADYL SOLUTIONS. Curve A, no additions. Curve B, H_2O_2 added. Curve C, EGTA and H_2O_2 added. (For all curves, vanadium concn. 69 micrograms per ml.; pH 1.70)

sample. Iron(III) interferes by forming a colored complex with EGTA and titanium(III) by reacting with H_2O_2 to form $\text{TiO}_2(\text{SO}_4)_2^{-2}$ and H_2TiO_4 . The interference of moderate amounts of iron and titanium is easily resolved by addition of fluoride ion. Moderate amounts of other metals and minor amounts of tungsten(VI) do not interfere. It is noteworthy that fluoride ion does *not* decrease the absorption of the vanadium complex formed in the presence of EGTA; this is in contrast to the action of fluoride in the classical method employing vanadyl ion and H_2O_2 only.

As sulfate, phosphate, nitrate, bromide, chloride, ammonium, sodium, and potassium ions do not interfere, a great variety of reagents can be employed for a dissolution of the sample and also for pH adjustment. In view of the limited interferences, the method is applicable to the determination of microgram quantities of vanadium in complex materials.

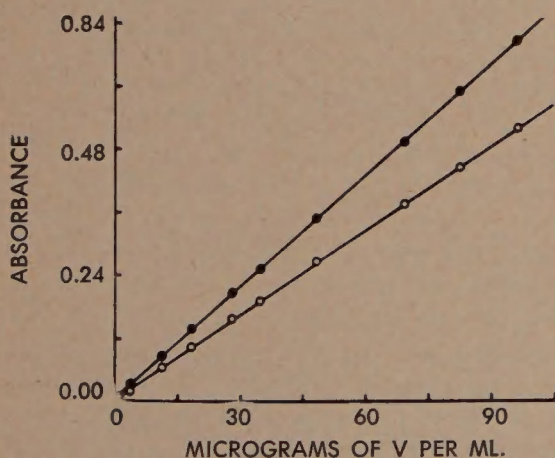


FIGURE 2. TYPICAL STANDARD CURVES. Upper, spectrophotometric (426 millimicrons); lower, photometric (Ilford No. 601 filter).

Results & Remarks. As indicated by the standard curves of Figure 2, Beer's law is obeyed in the range 3 to 120 micrograms of vanadium per milliliter in the photometric

method and 1 to 120 micrograms per milliliter in the spectrophotometric method. Under the conditions of the procedure, the maximum intensity of the absorption is not attained until 25 minutes after the mixing of all of the reagents. This delay may be associated with the slow rate of oxidation of the vanadyl ion by hydrogen peroxide; at least the maximum absorbance is reached more rapidly if the final solution is warmed to 50° . The yellow-orange solution complex, once formed, is completely stable and the absorbance of the final solution was found to be unchanged 8 days after preparation.

Acknowledgment. J. R. Geigy, A-G., Basel, is thanked for the EGTA used in this work.

This is paper XX in the series "Analytical Applications of the Chelons." Papers XVIII and XIX are to be presented 8th Latin American Congress on Chemistry, Mexico, March, 1959.

Reference. (1) Bermejo Martinez, F., Prieto Bouza, A., *Inform. quim. anal.* 11, 58 (1957).

[Rec'd 12Jan59]

Preparation and Purification of Dimethyl Oxalate for Use in Precipitation from Homogeneous Solution

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Dimethyl oxalate has been recommended as a source of oxalate ions for the precipitation from homogeneous solution of calcium (1), thorium (2, 3), rare earths (4-7), and actinium (8). Methods devised (9-12) for the preparation of dimethyl oxalate are generally tedious and complex, and in some instances require the use of dehydrating agents. Commercial dimethyl oxalate often contains an excess of oxalic acid. The presence of unreacted oxalic acid renders the product undesirable for use in precipitation from homogeneous solution.

Carron and co-workers (3) prepared dimethyl oxalate by the simple reaction of oxalic acid with reagent grade methanol. The ester was not isolated and the methanolic solution was employed directly. Unfortunately, unreacted oxalic acid remains in Carron's preparation. The present authors have now modified this method in order to prepare a product nearly free of oxalic acid.

— TABLE I. % FREE OXALIC ACID IN —
DIMETHYL OXALATE

Dimethyl oxalate source	% free oxalic acid*
Present method (Batch I)	4.35
Present method (Batch II)	3.72
Present method (Batch II, recrystd.)	0.66
Product from Co. A	1.74
Product from Co. B (Lot I)	10.5
Product from Co. B (Lot II)	12.5

* % free acid (as oxalic acid) by potentiometric titration with NaOH in methanol.

Procedure. Heat reagent grade oxalic acid dihydrate in an oven at 100° for 3 hr. Break up the crust and heat at 100° for an additional hour. Dissolve 40 g. of the cooled product in 100 ml. of reagent grade methanol. Allow the methanolic solution to stand at least 3 days, then cool to 0° thus crystallizing the dimethyl oxalate and leaving unreacted oxalic acid in solution. The yield is 45 per cent.

The melting point of the ester was found to be in the range of 53.5–54.2° which compares favorably with the literature. The oxalic acid content of the product can be reduced significantly by one recrystallization from reagent grade methanol.

Results & Remarks. The free acid in the product obtained by the above procedure was determined by potentiometric titration in reagent grade methanol at 7°, the methanolic solvent and low temperature being employed in order to diminish the hydrolysis of the ester. A 0.1069 N solution of sodium hydroxide in reagent grade methanol, standardized against potassium acid phthalate, served as the titrant. The free acid content of commercial dimethyl oxalate was also determined. The results in Table I show that a product low in oxalic acid can be obtained by this method and especially after one recrystallization from methanol. The results are calculated in terms of oxalic acid content and therefore represent an upper limit because methyl hydrogen oxalate is likely to be present.

Acknowledgment. This work was supported in part by U. S. A. E. C. Contract AT-(11-1)-582.

References. (1) Gordon, L., Wroczynski, A. F., *Anal. Chem.* 24, 896 (1952). (2) Kall, H. L., Gordon, L., *ibid.*, 25, 1256 (1953). (3) Carron, M. K., Skinner, D. L., Stevens, R. E., *ibid.*, 27, 1058 (1955). (4) Willard, H. H., Gordon, L., *ibid.*, 20, 165 (1948).

(5) Gordon, L., Vanselow, C. H., Willard, H. H., *ibid.*, 21, 1323 (1949). (6) Gordon, L., Barndt, R. H., Quill, L. L., Salutsky, M. L., *ibid.*, 23, 1811 (1951). (7) Banks, C. V., Edwards, R. E., *ibid.*, 27, 947 (1955). (8) Salutsky, M. L., Kirby, H. W., *ibid.*, 28, 1780 (1956). (9) Bow-

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(10) Rising, M., Stieglitz, J., *J. Am. Chem. Soc.* 40, 726 (1918). (11) Reimer, M., Dounes, H., *ibid.*, 43, 950 (1921). (12) Dutt, P. K., *J. Chem. Soc.* 1923, 2714. [Rec'd 20Oct58]

Thermochromic Detection of the Acetonyl Grouping in Organic Compounds

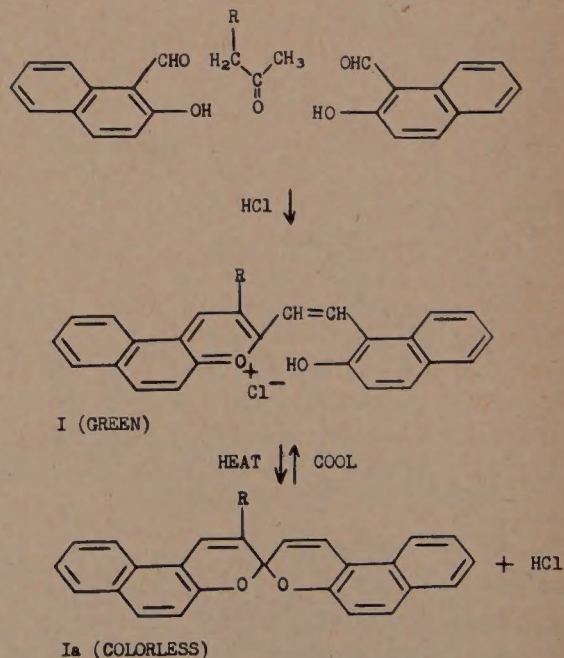
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Thermochromic color tests for the detection of particular organic groupings are little known. Specific color tests for aliphatic ketones are also apparently uncommon. The few known tests usually give positive results with other types of carbonyl compounds, such as acetophenone or acetaldehyde (1).

The atmosphere contains many types of carbonyl compounds for which straightforward methods of determination are desirable. Photometric determinations could result from a quantitative study of simple, sensitive, and specific color tests. The thermochromic color test presented in this paper is relatively simple, is sensitive in most cases, and (with the exception of a few cycloalkanones) is specific for the acetonyl (CH_3COCH_2 -) grouping.

This test is based on the following reactions:



This mechanism appears to be correct, for the present workers have found that the authentic compound Ia ($R = n$ -hexyl), prepared after Dilthey (2), undergoes the identical color reactions.

Reagents & Equipment. 2-Hydroxy-1-naphthaldehyde, 0.5% in anhydrous methanol; HCl, anhydrous gas; *o*-dichlorobenzene. For wavelength measurements, a Cary Model 11 recording spectrophotometer was used.

Test Procedure. To 0.1 ml. of the methanolic test solution in a 15-ml. centrifuge tube add 0.5 ml. of the 0.5% methanolic solution of 2-hydroxy-1-naphthaldehyde. Gently agitate this mixture with a jet of HCl gas for 30 sec. If aliphatic ketones are present at high concentrations, the mixture becomes dark blue-green. Add 0.5 ml. of *o*-dichlorobenzene. Vigorously boil the mixture until all of the methanol but none of the *o*-dichlorobenzene are distilled from the mixture. Heat the sides of the tube first so that this distillation is accomplished quickly and cleanly. Cool the remaining liquid. A brilliant green color (usually with a wavelength maximum at 650 millimicrons) which fades and almost completely disappears on heating and reappears on cooling indicates the presence of aliphatic ketones containing the acetyl group. Also run a reagent blank.

Test Results. Positive results were obtained with the following compounds (and with the sensitivity in micrograms): acetone (1), 2-butanone (0.3), 2-pentanone (1), 2-hexanone (0.2), 2-heptanone (0.2), 2-octanone (0.2), 2-undecanone (1), 2-tridecanone (1), 2-heptadecanone (1), 2-nonadecanone (1), phenylpropanone (100), cyclobutanone (4), cyclopentanone (0.2), cyclohexanone (5), acetylacetone (1), acetonylacetone (1).

The following compounds gave negative results: formaldehyde, biacetyl, 3-pentanone, 3-heptanone, 4-heptanone, 1,3-diphenylpropanone, acetophenone, 2-acetylnaphthalene, 4-acetylbiphenyl, acetaldehyde, *n*-heptaldehyde, cyclohexanol, phenol, and pyrene.

Remarks. From the test results it is apparent that aliphatic ketones containing the CH_3COCH_2 - grouping give a very sensitive and selective color reaction. The only exceptions are cyclobutanone, cyclopentanone, and cyclohexanone, which also give a positive, green reaction. Various other types of carbonyl compounds do not give a positive test. It should be emphasized that a positive test consists of a *reversible* color change involving a yellow, pink, or pale green color at the boiling point and a brilliant green color at room temperature.

References. (1) Feigl, F., "Spot Tests in Organic Analysis," Elsevier, N. Y., 1956, pp. 223-225. (2) Dilthey, W., Wübken, H., *Ber.* 61, 963 (1928).
[Rec'd 27Aug58]

Spectrophotometric Determination of Microgram Quantities of Molybdenum in Uranium Trioxide Using Dithiol

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A rapid, spectrophotometric method for the determination of molybdenum in uranium trioxide has been developed. The procedure makes use of the yellow-green complex formed between molybdenum and dithiol (toluene-3,4-dithiol) in hydrochloric acid solution. This complex is extracted with carbon tetrachloride and is then measured spectrophotometrically.

Preliminary Studies. Hydrochloric acid was the best solvent for uranium trioxide. Since it was necessary to use up to 50 g. of sample per determination, 100 ml. of 1:1 hydrochloric acid was used to give rapid and complete solution of this amount of sample. Various solvents were tried for the extraction of the molybdenum-dithiol complex. Butyl acetate, which has been recommended (1), extracted some of the yellow uranyl chloride, which partially masked the yellow-green color of the extracted complex. Carbon tetrachloride was found to extract the molybdenum complex quantitatively, without extraction of any uranyl chloride.

It was found necessary to add a reducing agent just prior to the addition of the dithiol, in order to obtain full development of the molybdenum complex. Reducing agents tried were sulfur dioxide, thioglycolic acid (2), ascorbic acid and hydrazine sulphate; only the last allowed full complex development. The effect of temperature on the formation of the complex was studied, and 30-35° was found to be the most satisfactory.

Reagents. *Dithiol soln.* Warm a 1-g. ampoule of dithiol until the reagent is liquified, then dissolve in 500 ml. of 1% (w/v) NaOH soln.

Other reagents include 1:1 (w/v) HCl; reagent grade hydrazine sulfate; reagent grade CCl_4 .

Procedure. Weigh a uranium trioxide sample containing 2-8 micrograms molybdenum. Add 100 ml. 1:1 HCl. Warm to effect solution and transfer to a 125-ml. separatory funnel. Adjust the temperature of the solution to 30-35°; add 0.2-0.3 g. hydrazine sulfate and shake to dissolve. Pipette 2 ml. dithiol soln. into the funnel, mix, and allow to stand 10 min. Pipette 10 ml. CCl_4 in the funnel, shake vigorously 1 min. Allow the phases to separate. Filter the lower phase through dry filter paper. Measure the absorbancy of the filtrate at 670 millimicrons using 1-cm. cells and a carbon tetrachloride blank. Calculate the molybdenum from a calibration curve.

Calibration Curve. Dissolve 0.1840 g. reagent grade ammonium molybdate in water and dilute to 1 liter. Pipette 10 ml. of this solution into a 1-liter

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TABLE I. RECOVERY OF ADDED
MOLYBDENUM FROM URANYL CHLORIDE SOLUTIONS

Micrograms, Mo		Micrograms, Mo	
added	recovered	added	recovered
1.00	1.00; 1.00	7.00	7.00; 7.00
3.00	2.97; 3.01	8.00	8.01; 8.00
5.00	5.00; 4.98	10.00	9.98; 9.98

volumetric flask, and dilute to mark. (One ml. of the final solution contains 1 microgram molybdenum.) Carry portions of 2, 4, 6, 8, and 10 ml. of the final solution through the procedure. Plot the absorbancy *vs.* micrograms molybdenum. Beer's Law is obeyed.

TABLE II. DETERMINATION OF
MOLYBDENUM IN URANIUM TRIOXIDE

Sample	Sample wt., g.	Mo ppm.
A	50	0.12; 0.13; 0.10; 0.10; 0.10
B	50	0.10; 0.10
C	10	0.26; 0.24; 0.24; 0.24
D	20	0.15; 0.16

Results. Table I shows the recovery of molybdenum added to uranyl chloride solutions. Table II presents some typical results obtained with samples of high purity uranium trioxide. Because tungsten could not be detected in these samples by the method described by North (3), it was unnecessary to consider an interference by tungsten.

References. (1) Sandell, E. B., "Colorimetric Determination of Traces of Metals," 2nd ed., Interscience, New York, 1950, p. 459. (2) Johnson, W. C. (Editor), "Organic Reagents for Metals . . .," Hopkins & Williams, Ltd., 5th ed., London, 1956, p. 74; also Chem. Publishing Co., New York, 1st Am. ed., 1956, p. 73. (3) North, A. A., *Analyst* 81, 660 (1956). [Rec'd 1Aug58]

Detection of Beryllium with Acetylacetone

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Beryllium acetylacetonate, which was first prepared by Combes (1) and described crystallographically by Jaeger (2), has been recommended for the microscopical detection of beryllium (3, 4). Difficulty has been experienced in obtaining good crystals by joining drops of beryllium acetate and acetylacetone on a slide by means of a platinum wire (5). Pure acetylacetone spreads over the slide. When it is added directly to a drop of a beryllium salt solution there is an immediate formation of oily drops, great

agitation, and separation of crystalline masses of right-angled plates upon standing. Dilution of the solution retards the appearance of these masses and does not produce better individual crystals. A procedure that gives a satisfactory test has now been developed and the effects of foreign ions have been examined.

Reagents include beryllium in the form of analyzed sulfate or nitrate, and satd. aq. acetylacetone soln. prepared from redistilled acetylacetone.

Procedure. Place a test drop on a slide and invert over a small crucible containing concd. aq. NH_3 . Remove the excess liquid from the $\text{Be}(\text{OH})_2$ precipitate with a fine-tipped capillary. Treat the washed residue with a small amount of satd. aq. soln. of acetylacetone. Add only enough solution to dissolve the $\text{Be}(\text{OH})_2$ precipitate. Beryllium acetylacetonate is soluble in excess acetylacetone, and an excess of the latter would delay precipitation and hinder the formation of characteristic individual crystals. When either a collection of oily droplets appears or crystallization begins at the edge of the drop of liquid, draw a fine-tipped glass rod through the oily or crystallized area and across the drop. Crystallization will follow the path of the rod. A positive test consists of the formation of characteristic right-angled plates, observable under 50x magnification.

Results. The limit of sensitivity, at which consistently positive tests were obtained, was 0.1 microgram of beryllium. A positive test was sometimes obtained with 0.05 microgram. Tests for the effect of 10 times as much foreign ion were run with both 0.5-microgram and 1-microgram amounts of beryllium and with 5 micrograms and 10 micrograms of various foreign ions present, respectively. Positive tests were obtained with some foreign ions when they were present in one of these amounts, but not the other. However, only tests which were positive with both amounts are considered as free from interference.

Ions of the following elements did not interfere with the identification of beryllium by the above procedure: Sb(III), As(III), Ba, Cd, Ca, Cs, Co(II), Cu(II), Dy, Er, Eu, Gd, Ge(IV), Au(III), Hf, Ho, Ir(III), Pb, Li, Lu, Mg, Hg(I), Hg(II), Mo(VI), Ni, Os(VIII), Pd(II), Pt(IV), K, Re(VII), Rb, Rh(III), Se(IV), Ag, Na, Sr, Te(IV), Tl(I), Th(IV), Ti(III), Ti(IV), W(VI), U(VI), V(V), Y, Zn. Although in some cases other precipitates were formed, the characteristic beryllium crystals were plainly distinguishable. Interferences were observed with ions of the following elements: Al, Bi,

As(V), Ce(III), Cr(III), Ga(III), In(III), Fe(III), La, Mn(II), Nd, Pr, Ru(III), Sm, Sc(III), Tm, Sn(II), Sn(IV), Zr(IV).

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Construction of Thread-Type Salt Bridge and Immersion-Type, Silver-Silver Chloride Electrode

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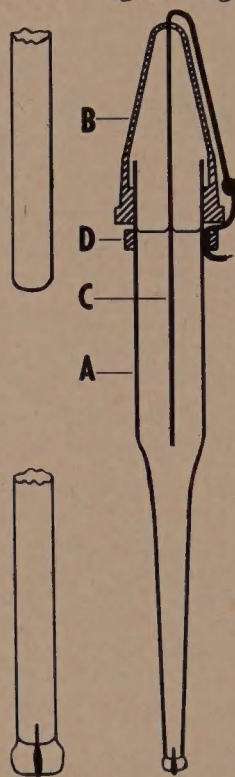
The preparation of potentiometric salt bridge junctions, by fusing an asbestos thread through the end of a piece of glass tubing, is simple with soft glass of diameter up to 3 mm. (1). When the tube diameter is larger, the operation is however sometimes unsuccessful, and more so if borosilicate glass is used. Often imperfect seals are obtained giving unacceptably, high leak rates and the hot flame required may burn off the tiny asbestos thread.

Such difficulties are easily surmounted by a simple "pinching" technique, which nearly always produces a satisfactory seal. Additionally, a leak path is thereby obtained that is several millimeters long, so that a thicker thread may be used without producing a high leak rate. Suitable threads about 0.5 mm. in diameter and 10 mm. long are obtained either by partially unravelling asbestos string or by twisting together long-fiber, filtering asbestos. In either case, the asbestos should be soaked in dilute hydrochloric acid, well washed and thoroughly dried. This thread-type salt bridge can be made part of an integrated design for an immersion silver-silver chloride electrode and salt bridge, shown in the right figure of the illustration.

Glass Blowing Operation. By rotation in a blow-pipe flame, symmetrically collapse one end of a length of 6-mm. outside tubing to an opening of

about 1 mm., as shown in the upper left figure. Cool to just the softening point, then insert an asbestos thread, leaving only about 3 mm. projecting. Reapply heat, keeping the projecting thread as cool as possible, and rotate until the tube has collapsed on to the thread. Remove from the flame and momentarily nip the end of the tube with a pair of pliers. The end of the tube should be flattened as shown in the lower left figure, so that the "pinch" is 2 to 3 mm. long. Undue force should not be used, but the thread should be well flattened; harder pinching lowers the leak rate but increases the electrical resistance. Since the projecting thread is brittle, snip off flush with the glass before using the bridge.

Assembly of Ag-AgCl Electrode. Draw the body A



of the integrated Ag-AgCl reference electrode (see right figure) and salt bridge from a 10-mm. semimicro test tube, and pinch an asbestos thread into the lower end by the above technique. With a red-hot sewing needle pierce a tiny hole in Cap B, a molded rubber bulb (e.g., Will Corp., Cat. No. 23261). (Before use, boil the cap in a dilute NaOH soln. and rinse well.) Employ a 100-mm. length of No. 24-gauge pure silver wire, C, as the electrode proper. Solder one end to a length of subminiature, plastic-coated, stranded copper connecting wire, and thrust the other end through the hole in the cap. Anodically coat the silver wire with silver chloride for a length of about 25 mm. Complete the assembly by introducing saturated KCl soln. to about the level shown, taking care to dislodge air bubbles. Grip the connecting wire by rubber band

D, which is cut from tubing, in order to prevent drag on the soldered joint. This electrode can be conveniently mounted alongside a suitable indicator electrode by use of a "V-notch" holder previously described (2).

Remarks & Results. After practice in the glass blowing operation, a fair degree of reproducibility can be achieved. When a batch of six moderately-pinched salt bridges were filled with saturated potassium chloride solution, the resistances all fell within the limits of 3000 to 5000 ohms. The resistances of a few bridges made with greater pressure were about five times greater. Under a head of 100 mm. of saturated potassium chloride solution. the leak rates of the former bridges

ranged from 0.03 to 0.05 ml. per hour; the rates for the high-resistance bridges were of the order of 0.01 ml. per hour.

Narrow salt bridges for microtitrimetry can be constructed by the "pinch" technique using somewhat finer asbestos thread.

Acknowledgment. This work was supported in part by the U. S. Atomic Energy Commission.

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EDTA Titration of Copper in Copper Linoleate

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Copper linoleate containing about 10 per cent copper finds extensive use in the manufacture of an anti-fouling, hot plastic ship-bottom paint. Six or seven hours are required for duplicate copper determinations when the electrolytic method given in the U. S. specifications is employed (1). This tedious method involves careful ignition of a weighed sample, solution in dilute surfuric acid and electrolytic deposition on a weighed platinum electrode. This investigation was undertaken to develop a useful and rapid supplementary determination of copper that would be applicable to the production control of this type of paint.

Various methods for the determination of copper based on an ethylenediaminetetraacetate (EDTA) titration have been reported (2). Pokorny and Pribyl (3) have determined copper in organic salts by dissolving the sample in chloroform, extracting the copper with 1:1 nitric acid and diluting the aqueous layer to a known volume. Murexide was used as the indicator for the EDTA titration of the copper in an aliquot of the final solution. An acid hydrolysis employing 10 per cent hydrochloric acid was used by Leggieri (4) for the extraction of metals from their organic salts prior to an EDTA titration.

Attempts were made to determine copper in copper linoleate according to the procedure

of Lucchesi and Hirn for the determination of the metal content of driers (5). This method does not require a hydrolysis step and uses a back-titration with Eriochrome Black T as indicator and zinc chloride as the back-titrant. However, the application was not feasible in this case because of the failure to observe an end point. A combination of dioxane and dilute hydrochloric acid was tried without filtration, followed by a direct EDTA titration with 1-(2-pyridylazo)-2-naphthol (PAN) as indicator, but inconsistent results were obtained.

In the method developed by the present workers, the copper is extracted expediently by acid hydrolysis with 1:3 nitric acid. After filtration the copper content of the solution is titrated with EDTA to an excellent and reproducible end point with PAN (6-7). Appropriate conditions for this titration are obtained by the addition of glacial acetic acid to the neutralized solution.

Reagents. *EDTA soln.*, 0.01 M. Dissolve 3.722 g. disodium ethylenediaminetetraacetate dihydrate and dilute to 1 liter with water. Store in a polyethylene or borosilicate glass bottle. (If desired, standardize under the conditions of the titration step of the procedure below.)

Other reagents include 0.1% methanolic PAN indicator soln.; 1:3 HNO₃; glacial acetic acid; 1:3 aq. NH₃.

Procedure. Weigh out about 0.15 g. copper linoleate to the nearest 0.1 mg. into a tared 100-ml. beaker. Add 10 ml. 1:3 HNO₃, cover with a watch glass and heat just at the boiling point until the copper is completely in solution. (The boiling time required for solution varies from 10-30 min. depending upon the nature of the sample.) Filter the mixture through retentive, quantitative filter paper into a 250-ml. beaker, washing well with hot water and not allowing the filter to run dry.

Add 1:3 aq. NH₃ to the filtrate until an intense blue or green color begins to appear. Test with pH paper. Add more aq. NH₃ dropwise until the pH is 7. Add 1 ml. of glacial acetic acid. The volume of the soln. should be about 125 ml. Add 6 drops of 0.1% PAN soln. and titrate with 0.01 M EDTA to a yellow-green color. As recognition of the end point may require practice, a comparison soln. (6 drops of dye to about 125 ml. acidified water) may be employed. The copper content is given by the following expression: Per cent Cu = (6.354) (ml. EDTA soln.) (molarity of EDTA) ÷ sample wt. in g.

Results & Remarks. Copper linoleate from three different sources was analyzed both by the above EDTA titration procedure and

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TABLE I. DETN. OF CU IN CU LINOLEATE

Sample	Per cent copper by	
	EDTA titration	electrodeposition
A	9.76; 9.81; 9.86	9.81; 9.91
B	9.99; 10.0; 10.0	10.0; 10.1
C	10.2; 10.3; 10.3	10.3; 10.3

by the electrolytic method (1). The results listed in Table I show that the EDTA and electrolytic methods are in close agreement. Duplicate determinations following the above procedure can be completed in about 1 hour. It should be emphasized that both the electrolytic and the EDTA titration methods determine the *total* copper in the sample whether or not present as copper linoleate or as such impurities as metallic copper or copper oxide.

Acknowledgment. Dr. O. Grummitt of Western Reserve Univ. is thanked for helpful suggestions.

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Rapid Determination of Readily Soluble Magnesium in Soils

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Recently, Edson and Mills (1) applied and extended the method of Taras (2) for magnesium in waters to the determination of magnesium in sodium acetate extracts of soils. They pointed out that there are distinct advantages in the use of Brilliant Yellow dye as a chromogenic agent in that iron and aluminum in relatively small amounts are without affect on it, and that furthermore, the presence of calcium intensifies the test color. These authors prepared the Brilliant Yellow solution with saturated lime water in order to adjust the pH and simultaneously to compensate for the calcium error. However, they make no mention of an appropriate color stabilizer, without which the color lake immediately commences to precipitate. In the course of further investigation, the

present authors tried polyvinyl alcohol, which several authors had already used successfully. The results were satisfactory and led to the procedure given in this paper.

The most common method of extracting exchangeable or "available" magnesium is the use of 1 N ammonium acetate in the ratio of one part soil to ten parts of solution. Such an extract was consequently tried but it was found that color development did not take place unless the extracting solution was of a normality of 0.1. In view of this, an extracting solution of 0.05 N sulfuric acid was substituted. This reagent has been successfully used by Beater (3) for the determination of available plant foods, the procedure for which has been improved by Biesenbach (4).

For the determination of magnesium in soils, the extracting solution of 0.05 N sulfuric acid produced extremely contrasting colors with Brilliant Yellow. The color development was also superior to that obtained with the use of 1 N sodium acetate as the extracting solution.

Reagents. Magnesium standards. Weigh out 3.058 g. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and dissolve to 1 liter with 0.05 N H_2SO_4 soln. (1.4 ml. concd. acid per liter). On the basis of the method outlined below, 1 ml. of this solution is equivalent to 10,000 lbs. MgO per acre. Take appropriate volumes of this stock solution and dilute to 500 ml. with 0.05 N H_2SO_4 in order to prepare a series of standards of 250, 750, 1,250 and 2,000 lbs. MgO per acre.

Lime water. Shake well an excess of calcium hydroxide or oxide with distilled water in a stoppered bottle and allow to stand overnight. Syphon off the clear solution.

Brilliant Yellow reagent. Weigh 0.01 g. Brilliant Yellow (C.I. 24890) and dissolve in 50 ml. methanol. Also weigh 30 g. of commercial 12% polyvinyl alcohol soln. or its equivalent in water and add to it with stirring 50 ml. water. Add this 4.5% polyvinyl alcohol soln. with stirring to 900 ml. lime water in a 1.5-liter beaker. Finally, add the Brilliant Yellow soln., and transfer the stirred mixture to a stoppered bottle.

Other reagents. Aluminum sulfate (0.08 g. of the hydrated salt in 100 ml. water); ammonium sulfate (10 g. in 100 ml. water).

General Procedure. Place a 2.5-g. sample of air-dry, 2-mm. mesh soil into a 50-ml. conical flask. Add 25 ml. 0.05 N H_2SO_4 and shake vigorously by hand for 1 min., and transfer immediately to a filter pad consisting of asbestos pulp between two filter papers on a Buchner funnel under vacuum. Take 1 ml. filtrate and add while rotating 15 ml. of Brilliant Yellow reagent. Allow to stand 20 min. and measure the absorption, using a green filter (560 millimicrons).

TABLE I. COMPARATIVE RESULTS

Soil type	Pounds MgO per acre		
	titrimetric	flame	colorimetric
Clansthal coarse sand	302	272	250
Shortlands clayey loam	2247	2271	2350
Inanda clayey loam	544	660	550
Dansland clayey loam	3155	2787	3450
Williamson fine sandy loam	695	803	800
Milkwood Kraal fine sandy loam	1068	1291	1220
Cartref coarse sandy loam	221	201	230

Standards are prepared by taking a 1-ml. volume of each appropriate magnesium standard soln., adding 1 drop of 0.08% aluminum sulfate soln. to approximate the small amount of aluminum in the soil extract which acts as a color intensifier, and 15 ml. of the Brilliant Yellow reagent. Allow to stand 20 min. and measure the absorption.

Procedure for Soils Containing Extractable Aluminum. Soils presenting a large amount of readily soluble aluminum are uncommon. However, when encountered, a cloudiness is occasionally observed following the color development due to the precipitation of aluminum. This interference can be circumvented as follows: Add 6 drops of ammonium sulfate to 5 ml. of the soil extract to prevent the precipitation of magnesium hydroxide. Add 5 ml. of lime water and allow to stand 10 min. Filter and use a 2-ml. aliquot of the filtrate in the general procedure.

Results. In order to establish the accuracy of the above method over a wide range of soil types, seven different Natal coastal soils were selected and the resulting 0.05 N sulfuric acid extracts analyzed for magnesium (a) by precipitation of magnesium ammonium phosphate, drying for 20 minutes at 60°, adding an excess of 0.1 N hydrochloric acid to dissolve the precipitate, and back-titrating the excess with 0.1 N sodium hydroxide with methyl orange as indicator, (b) by using a Beckman DU flame spectrophotometer, compensating for calcium and phosphorus, and (c) by the present photometric method.

The satisfactory results in Table I indicate a degree of correlation sufficiently accurate for agricultural advisory purposes. It is possible to employ the 0.05 N sulfuric acid extract for the determination of calcium and potassium by flame photometry.

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Solubility of Potassium Tetraphenylboron in Acetone-Water Solutions

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A variety of procedures have now been devised for the determination of potassium involving the initial precipitation of potassium tetraphenylboron. In some methods, this salt is then dissolved in acetone and subsequently titrated with an aqueous solution, and hence the acetone:water ratio of the final solution is critical.

In argentometric methods, for instance, sufficient water must be present to avoid solution of silver tetraphenylboron and yet sufficient acetone to effect solution of potassium tetraphenylboron. Some workers have recommended approximately 1:1 acetone-water for such procedures. Information on the solubility of potassium tetraphenylboron in this solvent system should help to define the appropriate concentration range more precisely.

Data on this solubility were obtained in a recent study of the degradation of soils and clay minerals by the removal of potassium with aqueous salt solutions. Sodium tetraphenylboron was used to precipitate the potassium, as released, thus enhancing its replacement. At the end of the degradation, acetone was added to dissolve the potassium tetraphenylboron, and the solution was filtered. The potassium content of the filtrate was subsequently determined. Because the amount of potassium tetraphenylboron involved was variable and frequently large, it became necessary to establish appropriate solution volumes and acetone:water ratios in order to ensure dissolution of this precipitate. The present article reports the solubility data developed incidental to this study.

Experimental Study. Acetone-water solutions were prepared by mixing the two solvents in definite proportions by volume. A volume basis was used in order that the results would be directly applicable in the degradation experiments. The concentration of acetone in these solutions was expressed as percentage by volume based on the combined volumes of acetone and water used. Reagent grade acetone was used and no attempt was made to determine or correct for the water present in it (0.5% max.). Potassium was precipitated from an acidified (HCl) solution of potassium chloride with sodium tetraphenylboron, filtered through paper, washed with water saturated with potassium tetraphenylboron, and air

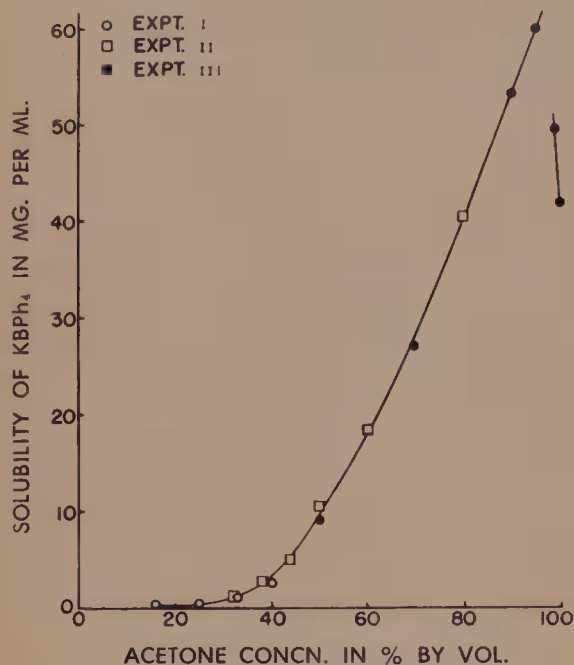


FIGURE 1. SOLUBILITY OF POTASSIUM TETRAPHENYLBORON IN ACETONE-WATER AT 28°C.

dried. The product was pulverized by gently rolling the filter paper cone during the drying process.

In the first experiment, samples of this pulverized, air-dried potassium tetraphenylboron were shaken intermittently for 16 hours with 20-ml. portions of the acetone-water solutions. In two further experiments, this salt was finely ground in a mortar and shaken with the solutions for 48 hours. In all cases an excess of the salt was added and the solutions were equilibrated to 28°C. The solutions were then either filtered or an aliquot of the supernatant was employed. Solutions containing 50% acetone or more in the second experiment were transferred to tared beakers, evaporated, and the amount of potassium tetraphenylboron present was determined by direct weighing. The potassium salt in the other solutions was destroyed with aqua regia and the potassium determined by flame photometry.

Results. The data thus obtained for the solubility of potassium tetraphenylboron in acetone-water solutions at 28°C. are given in Table I. Each value is the mean of two or more determinations. The values of Table I are shown graphically in Figure 1.

The increase in solubility observed when very small amounts of water are added to acetone is an interesting effect, previously unreported. It will be seen that the solubility of this salt rises sharply from a concentration of about 35% to about 95% acetone. These data make clear the desirability of maintaining as high an acetone:water ratio as appropriate in those analytical methods requiring

TABLE I. SOLUBILITY OF KBPh_4 IN ACETONE-WATER AT 28°C.

Acetone % by vol.*	KBPh_4 soly., mg./ml.†	Acetone % by vol.*	KBPh_4 soly., mg./ml.†
16	0.4 ^I	60	18.4 ^{II}
25	0.6 ^I	70	27.0 ^{III}
32	1.2 ^{II}	80	40.6 ^{II}
33	1.1 ^I	90	53.0 ^{III}
38	2.9 ^{II}	95	59.8 ^{III}
40	2.5 ^I	99	49.3 ^{III}
44	4.9 ^{II}	100	41.8 ^{III}
50	10.5 ^{II} ; 8.9 ^{III}		

* Uncorrected for H_2O content of reagent grade acetone (0.5% max.).

† Superscript numbers indicate Expt. no.; see text.

an acetonc solution of potassium tetraphenylboron. For comparison purposes, it may be noted that values for the solubility of potassium tetraphenylboron in pure water given in the literature include 0.046 and 0.053 mg./ml. at 20°, and 0.065 mg./ml. at 25°C.

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Acid-Base Indicator from Ratanjet Root

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When the ratanjat root (*Onosma echioides*), which is used as an antiseptic in the Indian system of medicine (1), is extracted with ether, a brown amorphous mass is obtained. An alcoholic solution of this extract showed distinctive color changes indicating the possible use of this material as an acid-base indicator. The color change is from pinkish-red in acidic solution to a bluish-violet in alkaline solution. The pH interval for the color transition is 7.5 to 8.8.

Titration with 0.1 and 0.01N sulfuric, acetic, and hydrochloric acids using ratanjat extract as indicator gave results fully comparable to those obtained with the use of phenolphthalein. The end point obtained in the titration of sodium hydroxide or acid solutions containing large amounts of either ethanol or acetone was sharper than that obtained in pure water solution. The end point obtained in the titration of alcoholic potassium hydroxide which had become yellow through storage was satisfactory with a green to red color change. The alcoholic solution of the indicator has a shelf life of at least

two weeks. Further study is in progress to determine the constituents of the extract, its use in mixed indicators, and its applicability to nonaqueous systems.

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Improved End Point by Addition of Polyvinyl Alcohol in the EDTA Titration of Calcium with Calcon as Indicator

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Lott and Cheng (1) described a stepwise ethylenediaminetetraacetate (EDTA) titration of calcium and magnesium based on titrating calcium at a pH above 12.5 with magnesium present as insoluble magnesium hydroxide, and then lowering the pH to 10 and titrating the redissolved magnesium. Calcon (2, 3) serves as the indicator for the calcium titration and Eriochrome Black T is added to sharpen the end point in the magnesium titration. The addition of a small amount of gelatin prior to addition of the Calcon was recommended to reduce the adsorption of this indicator on the magnesium hydroxide precipitate (1). This adsorption results in a slow end point. The superiority of Calcon over murexide and its suitability for the titration of calcium in the presence of substantial amounts of magnesium has now been confirmed (4, 5) as has the practicality of the stepwise titration procedure (6).

The authors have now found that addition of polyvinyl alcohol in place of gelatin is a far more satisfactory remedy to prevent the adsorption of Calcon. The end point thus obtained is not sluggish and, as the representative results given in Table I indicate, the accuracy of the calcium titration is not affected. It may also be noted that the polyvinyl alcohol has no effect on the course of the subsequent titration of magnesium.

Preliminary Study. Initially, glycerin and a quaternary ammonium salt were tried. However, they were less satisfactory than gelatin. Polyvinyl alcohol was then tried and was found to be a more effective protective colloid than gelatin at the high pH of the medium. Polyvinyl alcohol is far more effective if added before the magnesium hydroxide is precipitated.

TABLE I. TYPICAL RESULTS

Milligrams of Ca present	found	Milligrams of Mg present	Molar ratio Ca:Mg present
1.50	1.48	12.00	1:13.2
2.30	2.29	12.00	1:6.6
2.30	2.30	6.00	1:3.3
4.60	4.64	6.00	1:1.7
11.50	11.52	6.00	1.5:1
11.50	11.54	2.40	3.8:1

Reagents. Prepare a polyvinyl alcohol soln. by mixing 2.0 g. of a medium-viscosity type polyvinyl alcohol (Elvanol 71-24, Du Pont, or equivalent) with 200 ml. of boiling water in a homogenizer (Waring Blendor or equivalent). This solution is stable indefinitely. Other reagents required are given by Lott and Cheng (1).

Procedure. To the sample solution (containing up to a total of 0.5 millimoles of calcium and magnesium), add 2 or 3 drops of the polyvinyl alcohol soln. and adjust the pH to 12.5 or above with NaOH. Add 3 drops of 10% KCN soln. and 3 drops of Calcon indicator soln. Titrate with 0.01 M EDTA to a red to blue end point. Preferably, heat sample solutions of high magnesium content to about 60° before adding the indicator, and titrate while hot.

As given earlier (1), adjust the pH to 10 with 1 to 2 ml. of ammoniacal buffer, boil to effect dissolution of the magnesium hydroxide, and add 1 ml. of buffer and one drop of Eriochrome Black T soln. Titrate the hot solution with EDTA to a red to blue end point. (For resolution of heavy metal interferences, see the earlier paper (1)).

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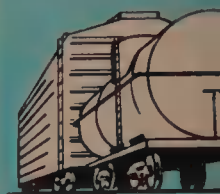
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Notes of Interest

Errata. September 1958 issue, page 67, 2nd line under "Reagents," change given value to "3.722 g." December 1958 issue, pages 106-108, for " δ -pyrones" read " γ -pyrones."

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What Are Emission Chemicals? A special group of J. T. Baker products known as emission chemicals finds use in the preparation of cathode coatings in many types of vacuum tubes. Alkaline earth oxides (*i.e.*, calcium, strontium, and barium oxides) are the most economical coatings giving high emission at lower temperatures at high efficiency. The usual oxide-coated cathode is obtained by placing the carbonate on the cathode and converting to the oxides by heating during the evacuation of the tube. For this use, these carbonates are usually termed emission chemicals.

For some purposes, especially if very long tube life is mandatory, a single carbonate or a mixture of two carbonates (*i.e.*, a so-called double carbonate or radio mixture) is preferred. Where a low activation level is important, a co-precipitated triple carbonate preparation finds extensive application in the formation of cathode coatings.

Baker's know-how to manufacture and to control emission chemicals—even in co-precipitated forms and as blended mixtures—so as to assure a desired range of particle size is important to the electronics industry. In order to assist this industry to achieve uniform production with a minimum of rejects, J. T. Baker blends all its emission chemicals offered in a powdered form to provide homogeneous lots of several thousand pounds. (This same type of blending is used to insure uniformity within each lot of many 'Baker Analyzed' Reagents.)

The further information given below delineates some of the emission chemicals offered by Baker and indicates the degree of purity and definition being achieved. More detailed information on these chemicals is available on request. Write Department CT, J. T. Baker Chemical Company, Phillipsburg, New Jersey.



in J. T. Baker BULK CHEMICALS

Triple Carbonate designates a co-precipitated product containing the three alkaline earth carbonates. The J. T. Baker Chemical Company offers triple carbonate preparations of both high calcium and low calcium content. The J. T. Baker specifications for each of these important products are given below.

	Triple Carbonate	
	Low CaCO_3	High CaCO_3
Barium carbonate	55.2 - 59.2%	54.0 - 58.0%
Strontium carbonate	36.8 - 40.8%	29.0 - 33.0%
Calcium carbonate	3.5 - 4.5%	11.0 - 15.0%
Water	0.10 % max.	—
Insoluble in HCl	0.01 % max.	0.010% max.
Water solubles	0.10 % max.	0.10 % max.
Chloride (Cl)	0.003% max.	0.003% max.
Sulfide (S)	0.001% max.	—
Heavy metals (as Pb)	0.003% max.	—
Iron (Fe)	0.003% max.	0.003% max.
Density (g/ml.)	—	0.70 - 0.90
Particle size range	1 - 10 microns	1 - 10 microns

Radio Mixture No. 3 is a *double* carbonate mixture composed of a 70:30 blend of equimolar co-precipitates of barium and strontium carbonates with sodium and ammonium carbonates, respectively, used as the precipitants. The specifications of J. T. Baker Radio Mixture No. 3 are given below.

Barium carbonate	55.2 - 59.2%
Strontium carbonate	40.8 - 44.8%
Water	0.10 % max.
Insoluble in HCl	0.010% max.
Water solubles	0.15 % max.
Chloride (Cl)	0.001% max.
Sulfide (S)	0.001% max.
Sodium (Na)	0.20 % max.
Heavy metals (as Pb)	0.002% max.
Iron (Fe)	0.002% max.
Particle size range	1 - 10 microns

Individual Carbonates. 'Baker Analyzed' Reagent Barium, Strontium and Calcium Carbonates are also purchased in bulk quantities by the electronics industry for the formulation of special emission coatings. The specifications for these reagent grade items are given in our recent Specification Catalog No. 58.

Suspension Forms of the carbonates finding specialized applications in filament coating are offered by J. T. Baker as Chemical R-500 and Chemical N-200. The former is essentially Radio Mixture No. 3 in butanol, butyl acetate, and pyroxylin cotton. The latter suspension was developed primarily for use by neon light fabricators.

Related Electronic Chemicals. In addition to the emission chemicals considered above, J. T. Baker makes available many solvents, salts, and acids required in the production of transistors and other components and materials of the electronics industry.

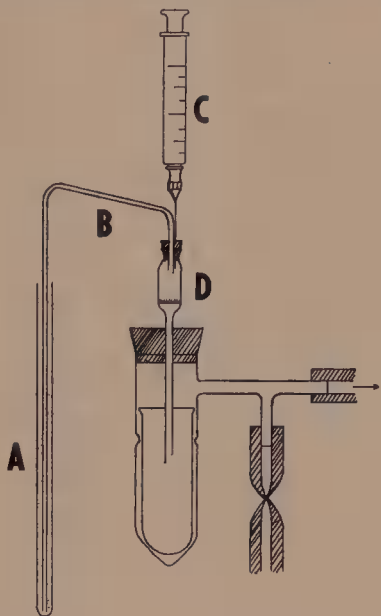
If you would like to receive a comprehensive list of the electronic chemicals currently produced by Baker in a high purity form and in bulk and tonnage quantities, write Department CT, J. T. Baker Chemical Company, Phillipsburg, New Jersey.

Expedient for Microfiltration

JOHN M. CORLISS

U. S. Army Chemical Warfare Laboratories,
Army Chemical Center, Maryland

A modification of the filtration apparatus used in gravimetric microanalysis has been devised which eliminates the troublesome adherence of particles of the precipitate to the walls of the pressure tube. Further, the modification allows the resumption of filtration through a clogged filter tube.



As illustrated, insert a 2-ml. syringe (C) by means of a 22-gauge hypodermic needle into the rubber stopper connecting the siphon (B) and the filter tube (D) in the apparatus of Niederl and Niederl [*"Micromethods of Quantitative Organic Analysis,"* Wiley, N. Y., 1942, p. 154]. A variable air space is thereby introduced above the solution in the pressure tube (A). Rapid plunger action in the syringe will produce agitation in the solution in the pressure tube thus freeing adhering particles and also hastening attainment of solubility equilibria so that wash volumes can be readily controlled.

A clogged filter tube often retards suction filtration until several drops of water are deposited on the filter. By withdrawing the plunger, the air volume in the siphon is decreased and the solution in the pressure tube can be drawn through the siphon until several drops are deposited on the filter, thus resuming filtration.

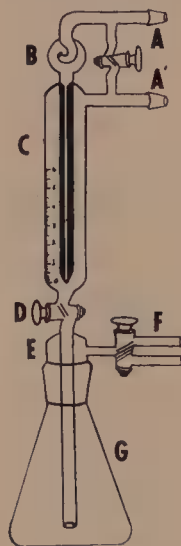
All-Glass Pressure Regulator

N. B. MEHTA*

Dept. of Chemistry, Central State College,
Wilberforce, Ohio

A sensitive and inexpensive manostat in which an increase or decrease in a reduced pressure can be effected while in operation can be constructed as illustrated. This apparatus has been used satisfactorily for continuous periods of operation up to six to eight hours. The use of a tapered capillary tubing in the regulator assures that non-condensable gases emerge at an even rate in very fine bubbles thus assuring constant equilibrium pressure during a fractionation and minimizing throttling changes and "suck-back" difficulties. Desired changes in reduced pressures can be obtained in small increments without upsetting the equilibrium conditions of the system. This apparatus can also serve as a leak detector.

Description. The apparatus consists of a calibrated regulator tube, C, 20 mm. in diameter and 100 mm. long. In the center of the regulator tube is affixed a capillary tube of 2-mm. bore, with a tip drawn to 1 mm. This capillary tube is connected through a safety trap, B, to a side arm, A, of 6-mm. tubing. A second side arm, A', attached to the top of the regulator tube, is connected through a 2-mm., angle stopcock to side arm A. This serves as a bypass system. Standard taper inner joints at A and A' are used to attach the manostat to the high vacuum system. The regulator tube, C, is connected to the mercury reservoir, G, through a 2-mm. bore stopcock, D, attached to 6-mm. diameter tubing which extends almost to the bottom of the reservoir.



The reservoir flask consists of a 125-ml. conical flask with attached 24/40 standard taper joint. An inner 24/40 standard taper joint, E, is attached by a ring seal to a stopcock, D, and is connected to services of vacuum and atmospheric pressure by a three-way stopcock, F, of 2-mm. bore. The apparatus can be rigidly clamped on a distillation rack by one clamp on the regulator tube and a ring with a wire gauze below the reservoir flask.

Operation. Side arm A' and one of the outlets of the three-way stopcock F are connected through an external three-way stopcock (not shown in the

* Present address: The Wellcome Research Laboratories, Tuckahoe, New York.

figure) to the source of vacuum. The other outlet of stopcock *F* is opened to the atmosphere when desired. At the start of the operation, the mercury is retained in reservoir *G*, stopcock *D* is kept closed, and the bypass stopcock connecting *A* and *A'* is opened. When the desired system pressure is achieved, the bypass is closed and stopcock *D* is opened slowly. Mercury is drawn into the regulator tube and is permitted to rise until the desired pressure is maintained.

When it is required to *increase* the reduced operating pressure in the system, stopcock *F* is opened to the source of vacuum and the mercury is withdrawn from the regulator tube. Stopcock *D* is then opened slowly. When a *decrease* in the reduced pressure is required, stopcock *F* is opened to the atmosphere and the mercury level in the regulator tube adjusted by manipulating stopcock *D*. At the end of the operation, the mercury, in order to reduce its contamination, should be drawn from the regulator tube into the reservoir. The bypass is then opened and the pressure in the system equalized to atmospheric pressure.

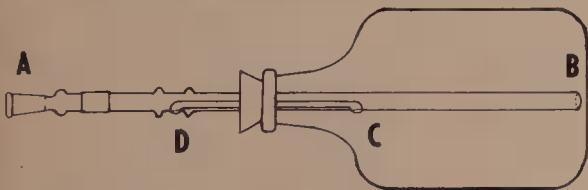
Multiple Sample, Continuous Dialyzer

J. B. STARK

U. S. Dept. of Agriculture, Albany, California

A large number of individual samples can be continuously dialyzed with the illustrated device which is described below. Either the dialyzed or residual fraction may be collected.

Assembly ■ Applications. A 5-gal. (Pyrex) bottle is mounted on a bottle roller and rotated at 0.5 to 3 rpm. Water enters the bottle near its base at point *B* via a 16-mm. glass tube, *A*, and leaves the bottle via the glass tube connecting point *C* to *D*. An appropriate rotating vacuum bearing permits circulation of water while the bottle is rotated. Solutions to be dialyzed can be poured into cellophane bags prepared in the usual manner. Rotation of the bottle tumbles the bags thus promoting dialysis.



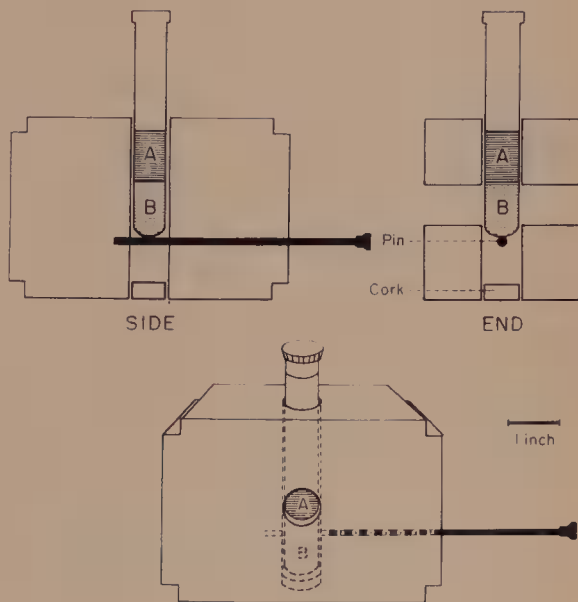
Sixteen bags of seamless cellophane tubing 1.27 inches in collapsed width and 24 inches in length were each filled with 30 g. of sucrose and 100 ml. of water and tied off. The filled bags were placed in the bottle which was previously filled with distilled water. After the tubing connections were made, the bottle was placed on the roller. A rotation rate of about 1 rpm. was used with a water flow of 200 ml. per min. The bags were removed at intervals and their contents analyzed. The sugar remaining in the bags at the end of 0, 2, 4, 6, 22, 30, and 46 hr. was respectively, 30, 18.9, 9.8, 7.5, 0.15, 0.028, and 0.010 g.

Test-Tube Adapter for Beckman DU Spectrophotometer

BENNIE IAK ■ L. A. WILLIAMS

Wayne State Univ., Detroit, Michigan

Several spectrophotometric procedures have been developed involving the concurrent measurement of colored complexes in two immiscible layers. This is usually accomplished by separating the two layers and then making absorption measurements of each layer independently. To obviate the separation of the layers, a test-tube adapter for the Beckman DU spectrophotometer was developed. The illustration represents a scale drawing of this adapter, which is easily fashioned from a wooden block. This device permits the determination of the absorption value of each of the layers of a two phase system where two colored derivatives of photometric interest are individually present.



The measurement of the bottom layer (*B*) is made with the pin in, as depicted in the side and end sectional views. Pulling the pin out as shown in the side (lower) view drops the cuvette down to the cork platform so that the upper layer (*A*) is in the light path. The cork insures that the cuvette in dropping does not break, and can be adjusted in height or size to compensate for the position of the meniscus between the layers. Screw holes in the block are unnecessary, since the block clamps firmly into place with the screws of the spectrophotometer riding in the edge notches (see illustration).

Any opaque cap, such as a sputum cup, can serve to exclude light through the top of the test-tube adapter. During extraction, centrifugation and measurement steps, the cuvette may be closed by a tight-fitting plastic stopper.

This test-tube adapter was designed during a study of the determination of copper and iron in a single sample by means of selectively substituted phenanthrolines. This adapter should be applicable to spectrophotometric methods where extraction is a necessary step prior to the spectrophotometric measurements.

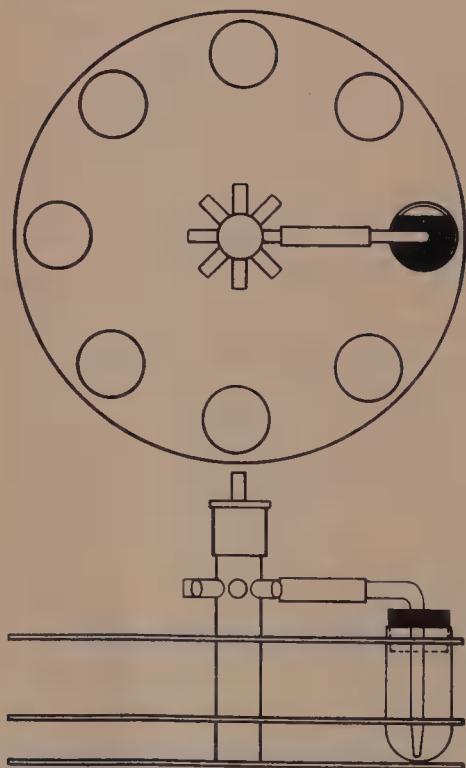
Acknowledgment. This study was supported in part by grant-in-aid, No. P-12, Receiving Hospital Research Corp.

Rotating Sample Table for Multiple Polarographic Analyses

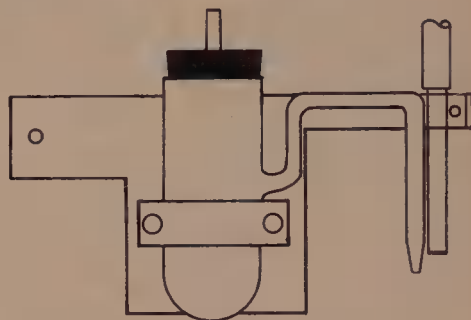
JAMES LUCK

Minneapolis-Honeywell Regulator Company,
Minneapolis, Minnesota

A simple "Lazy Susan" assembly designed to hold sample tubes for multiple polarographic analyses can be readily constructed as illustrated in top and side views with one sample tube and gas bubbling tube in position.



Mount three disks (of aluminum or other appropriate material) on a hollow, central metal shaft which rotates on a bearing near its top. The two top disks should have 25-mm. holes to accommodate the sample tubes. Solder several smaller metal tubes to the central shaft to carry nitrogen through rubber tubing to glass bubbling tubes in the sample tubes. While the polarogram is being recorded, the bubbling tubes can easily be raised from the sample solution so that the bottom of the rubber stopper rests on the rim of the tube.



The entire apparatus may be placed in a constant temperature bath. The half cell reference electrode and dropping mercury electrode may be mounted as a separate unit (see illustration) and be clamped to a ring stand. The electrode assembly is dipped into each sample tube as the Lazy Susan is rotated.

Visualization of End Point Color Changes in Titrimetry

J. E. BOLZAN

Laboratorio Químico-Metalurgico, Ferrocarril
General Roca, Remedios de Escalada, Argentina

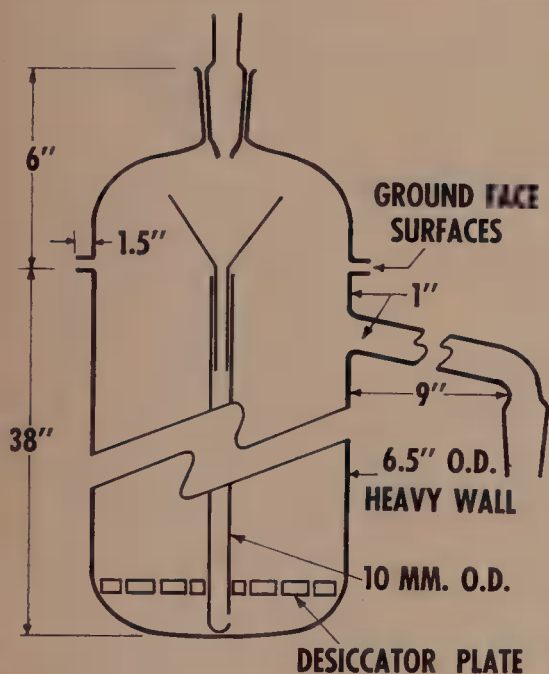
Taylor [*Anal. Chem.* 26, 620 (1954)] has described an "outrigger" flask for accentuating the color in iodimetric titrations using carbon tetrachloride to detect the presence of free iodine. A much simpler approach, which apparently has not been described in standard monographs, is to conduct the titration in a 50- or 100-ml. volumetric flask and to observe the color change in the narrow band of immiscible solvent (heavier than water) obtained by inverting the stoppered flask. This technique is also of utility in titrations of highly colored solutions employing soluble indicators. In this case, because a small volume is thus viewed, small color changes are more easily recognized.

All-Glass Extractor for Bulk Solids

BORIS WEINSTEIN ■ M. J. MITCHELL

Dept. of Chemistry, The Ohio State University,
Columbus, Ohio

Commercially available extractors for solids (*i.e.*, ground plant materials) are usually of Soxhlet design. They suffer from the disadvantages of fragility and small capacity when constructed of glass, and of corrosibility when built of iron, copper or brass. Stainless steel extractors, though not thus limited, are expensive. The continuous extractor illustrated is sturdy, inexpensive, easily constructed, and holds about ten pounds of finely ground material.



Operation. Insert the base plate (a 5.5-inch porcelain desiccator plate) and the glass center tube as illustrated. Cover the former with a 1-inch layer of glass wool. Add the material to be extracted until the level is about 3 inches below the outlet arm. (A glass wool pad may be inserted at 4-inch intervals to prevent channeling and packing.) Then place a glass wool plug on top of the material and weight it down with a second desiccator plate. Fill the extractor with solvent through a syphon connected to the center tube. Now insert the funnel and seat the ground-glass, hemispherical cover on top of the extractor. Fit this cover with a drip-tip reflux condenser and connect the side arm to a 2-liter flask containing more solvent. Begin the extraction by bringing the solvent in this flask to a boil. The vapors are carried up the side arm and are condensed and fall to the bottom of the extractor *via* the funnel and tube. This displaces some of the liquid which returns to the flask *via* the side arm. A continuous extraction is established.

To isolate the extract, remove the flask, the condenser, the cover, and the funnel and attach a syphon or suction system to the center tube. Combine the contents of the flask and the solution removed from the extractor and process as desired. (Of course, if desired, the flask contents may be used separately.) The material remaining in the extractor can be freed from residual solvent by blowing air through this tube. The solid may then be subjected to further extraction or it may be removed by inverting the extractor.

Method of Controlling the Rate of Addition of Liquids in Organic Reactions

ALFRED F. MEINERS ■ ALFRED L. SCHERER

Midwest Research Inst., Kansas City, Missouri

A device giving an accurate control of addition rate of liquids can be easily assembled. The assembly, as illustrated, consists of a graduated addition funnel from which the liquid is conducted down through a plastic tube to the drop regulator previously calibrated. The drop regulator, which is maintained half-full of liquid, consists of a glass tube ($\frac{1}{2}$ in. x 2 in.) stoppered on both ends. If desired, the drop regulator from an intravenous assembly can be used to advantage. The liquid flows down to the reaction mixture through a second plastic tube, which can be constricted by means of a screw clamp, and into the reaction mixture through a hypodermic needle inserted through a rubber stopper.



By adjusting the height of the graduated addition funnel and the amount of constriction of the plastic tube, a practically constant rate of addition is effected. An excess of reagent is usually placed in the addition funnel to maintain a more constant pressure. The flow rate through the drop regulator can be measured by observing the time required for a specified amount of liquid to pass through the device. A more convenient method involves counting the number of drops in a given volume and also the number of drops per minute. The flow rate can easily be altered by adjusting the screw clamp and observing the change in the flow rate through the drop regulator.

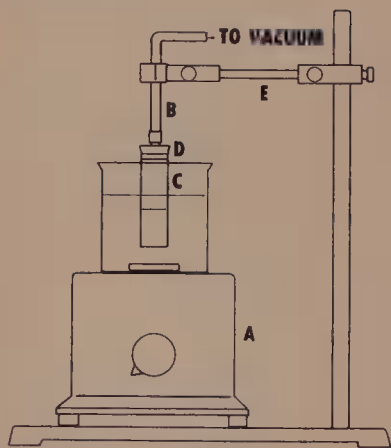
Simple Expedient for Evaporating Small Amounts of Solvent

ROBERT L. CLEMENTS

Dept. of Plant Biochemistry, Univ. of California,
Riverside, California

Micro procedures often require the evaporation of small amounts of solvent in the recovery of solutes. This can be speeded if a vacuum and heating and swirling can be effected concurrently. The illustrated expedient achieves this simply and effectively.

A vial, *C*, partially filled with the sample solution is suspended in a 250-ml. beaker on a magnetic stirrer, *A*, by a length of Tygon tubing ($\frac{1}{4}$ -in. outside diam.), *B*. The tubing is attached to the vial by a short length of glass tubing inserted into a neoprene stopper, *D*, and leads to the vacuum source (*e.g.*, water aspirator). Water at an appropriate temperature is placed in the beaker, the magnetic stirrer is started, and the vacuum is then connected.



If the water level is correctly chosen and if the vial is suspended at the proper depth, effective swirling of the vial contents results.

The frequency of the motion depends on the length of tubing between the vial and the clamp, *E*; the most effective motion is found by brief study. Use of a polyethylene beaker or a glass beaker lined with resilient material is advisable.

This expedient is especially useful for rapid evaporation of solvent from chromatographic fractions (3-10 ml. vol.) without bumping. By this technique 5 ml. of petroleum ether at 30° in a 2-dram vial is evaporated within 2 minutes.

Silicone Grease Removal from Glassware

GEORGE M. STEINBERG

U. S. Army Chemical Warfare Laboratories,
Army Chemical Center, Maryland

Triethylamine or other organic amines readily dissolve silicone greases even at room temperature. Hence, they can be used to remove silicone greases that are employed as lubricants for stopcocks and ground glass surfaces. It is also worthy of note that the solubility of the silicones is not limited to the amines so that the use of silicone greases in analytical procedures involving nonaqueous solvents should be regarded with caution.

Tricresyl Phosphate as a Heat Transfer Medium

GENE ROSENDAHL

National By-Products, Inc., Des Moines, Iowa

Many properties of *para*-tricresyl phosphate recommend its use as a heat transfer medium in laboratory applications such as high temperature baths. The properties of noninflammability, low volatility at high temperatures, and a boiling point of 420° make this compound superior to the commonly used mineral oils. There is no appreciable darkening after several months of continuous use at 110°, no odor after the first few hours of use, and no significant corrosion of the vessel. It must be stressed that the *ortho* isomer is *very* toxic, and hence an *ortho*-free grade of *para*-tricresyl phosphate should be used.

Holder for Small Volumetric Flasks

ROBERT S. ROUSE

Dept. of Chem., Lehigh Univ., Bethlehem, Pa.

A holder for small volumetric flasks is improvised by Menville [*Chemist-Analyst* 46, 73 (1957)] by fitting the bottom half of a rubber pipette bulb into a common cork ring. The flask is thereby gripped and held firmly upright. An alternative is to make use of a rubber (tapered collar type) filter adapter (*e.g.*, Arthur H. Thomas Co., item 5115-T). The filter adapter is fitted into a cork ring (3-in. outside diam., 2-in. inside top diam.). For a 5- or 10-ml. flask, use a #3 adapter; for a 25-ml. flask, a #4.



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Indicators for Nonaqueous Acid-Base Titrimetry. Part I

JOHN T. STOCK ■ WILLIAM C. PURDY

Dept. of Chemistry, Univ. of Connecticut,
Storrs, Conn. and Dept. of Chemistry, Univ.
of Maryland, College Park, Maryland

One of the striking features of analytical chemistry during the past fifteen years has been the increasing number of papers concerning nonaqueous acid-base titrimetry. The present review considers extensively the literature on indicators reported to be useful for the visual or photometric detection of the end point in such titrations and covers the period through June 1958. Electrometric and other instrumental methods of end-point detection have been reviewed elsewhere by the present authors (1-3). This first installment reviews the nature and history of the method, azo compounds as indicators, and (in part) triphenylmethane dyes. The concluding installment to appear in the June issue will have an addendum noting recent papers.

Nature of the Method

The potentialities of acid-base titrimetry in nonaqueous solution are now being fully realized. For example, substances which are insoluble in water or which are insufficiently active to be titrated in aqueous solution, may often be handled under essentially water-free conditions. Further, a mixture of two or more substances may sometimes be analyzed by a single "differentiating" titration in a suitable nonaqueous solvent, or by a series of titrations conducted in different solvents.

Solvents may be roughly divided into four types: aprotic, protophilic, protogenic, and amphiprotic solvents. Neutral substances like benzene, chloroform, and carbon tetrachloride are examples of *aprotic solvents*. They possess low dielectric constants, are chemically relatively inert, and do not cause the ionization of either acids or bases. Solvents of this type serve merely as vehicles and take no part in the acid-base reaction itself. *Protophilic solvents* are basic substances which react with an acid solute to form a solvated proton together with the conjugate base of the acid. Examples of such solvents are the ethers, dioxan, and the amines. Sulfuric acid is an example of a *protogenic*

solvent. Such acidic substances ionize the basic solute with the formation of the conjugate acid of the base. *Amphiprotic solvents* can exhibit both protogenic and protophilic characteristics and are liquids which are themselves ionized to a slight extent. Water, glacial acetic acid, and the alcohols are examples of this type of solvent.

Although a compound like phenol is very weakly acidic in water, dissolution in a strongly protophilic solvent such as ethylenediamine greatly enhances the apparent acidity, so that titration with, for example, sodium methoxide becomes perfectly feasible. In fact, ethylenediamine and similar solvents have so pronounced a *levelling effect* that, irrespective of their strength in water, all acidic substances appear to be strong acids in such solvents. The reverse is true of bases dissolved in protogenic solvents. Liquids like acetone, acetonitrile, etc., are valuable not only because of their excellent solvent properties, but also since their levelling properties are not too pronounced. This sometimes permits a differentiating titration of the components of an acidic mixture. Mixed solvents are often valuable. Thus sodium methoxide titrant is often put up in benzene-methanol. The benzene suppresses solvolysis and hence sharpens the end point. Glycol-hydrocarbon (G-H) solvents (glycol admixed with a suitable hydrocarbon, chlorinated hydrocarbon, or higher alcohol) are recommended for the titration of salts and soaps, owing to the satisfactory solvent power of the mixture for these substances.

Although nonaqueous titrimetry has never been treated comprehensively, various monographs and reviews treat certain aspects of the topic (4-28).

History of the Method

Certain coloring agents have been used for centuries as indicators of acid-base properties in aqueous systems; but it was generally supposed that analogous phenomena did not occur in water-free systems. This illusion was dispelled late in the 19th century and, over fifty years ago, Vorländer (29) studied the interaction of aniline and hydrogen chloride in benzene. The early history of nonaqueous acid-base titrimetry has been reviewed (30, 31).

Organization of the Review

The indicators considered are grouped according to chemical structure and within each group according to present importance. Many of the indi-

cators are well known, and only their indicator use in nonaqueous systems is considered here. Where given, Colour Index Numbers are those of the Second Edition (1957-1958). Within each section on a given indicator, all titrations mentioned were performed with that indicator unless otherwise qualified. Unless otherwise stated, all solvents referred to are essentially anhydrous. Fused-salt titrations are not considered in this review.

Azo Compounds

Indicators containing the azo linkage have found extensive use in nonaqueous acid-base titrimetry, particularly in neutral or basic solvents. The most important members of this group are azo violet, methyl orange, methyl red, and methyl yellow.

p-Aminoazobenzene, a simple azo compound, has been used as indicator in the microtitration of reserpine in chloroform with a chloroform solution of *p*-toluenesulfonic acid as titrant (32).

Azo Violet, 4-(*p*-nitrophenylazo)resorcinol, has been much used in titrations performed in dimethylformamide. The purification of this solvent has been discussed (33). This solvent and sodium methoxide in benzene-methanol have been employed in the titration of phenols (34), enols and imides (35), nitroguanidine and related compounds (36), hexahydro-1,3,5-trinitro-*s*-triazine (*i.e.* RDX) in wax, isobutylene, etc. (37), and acidic forms of substituted 5-amino-1,2,3-triazoles (38). Using the same solvent and potassium methoxide in benzene-methanol as titrant, phenolic groups have been determined in lignin preparations (39) and benzotriazoles (40). In the same solvent with tetrabutylammonium hydroxide in benzene-methanol as titrant, ammonium nitrate has been estimated in explosives (41). In all cases the indicator has been dissolved in benzene.

Weak polybasic acids like citric acid and weakly acidic substances such as phenols (42, 44), have been titrated in pyridine with tetrabutylammonium hydroxide. This titrant may be prepared from the quaternary iodide by reaction with silver oxide (43). In mixed solvents containing pyridine, phosphate in ergotoxine phosphate (45), 2-phenylquinoline-4-carboxylic acid (cinchophen) (46), and stilboestrol (47) have been titrated with potassium methoxide. In the titration of the sulfonamides of primary

amines, *n*-butylamine is a suitable solvent (48). The ionizing properties of ethylenediamine (49) and acidity in ethylenediamine-water mixtures (50) have been studied. Ethylenediamine has been evaluated in nonaqueous titrimetry (51) and employed in the titration of ammonium salts, aliphatic amines, etc. (52), and phenolic esters (53).

Methyl Orange, sodium *p*-dimethylaminoazobenzenesulfonate (C.I. 13025), has been used for the titration of alkali metal salts of weak, monobasic organic acids in "G-H" solvent. The titrant was hydrochloric or perchloric acid in "G-H" solvent (54). This titration has been applied to α -diethylamino-2,6-acetoxylydide (Xylocaine, Lidocaine) on a semimicro scale (55) and to morphine narcotics (56). A determination of α , β -unsaturated compounds has been accomplished by their catalyzed reaction with morpholine to form a tertiary amine; the latter is titrated with methanolic hydrochloric acid after destruction of the excess morpholine. In this method methyl orange is screened with xylene cyanol FF (C.I. 43535) (57).

Methyl Red, *p*-dimethylaminoazobenzene-*o*-carboxylic acid (C.I. 13020), has been employed in titrations in a wide variety of solvents. Additives such as antihistamines in aspirin-acetophenetidine-caffeine tablets have been titrated in chloroform with perchloric acid in dioxan solution (58). Caffeine has been determined by dissolution in a minimum amount of chloroform, addition of dioxan, and titration with perchloric acid (59). Increased solvent power and better end-point detection have been claimed for the solvent system phenol-chloroform-acetonitrile. This system has been applied in the titration of codeine phosphate and of salts of other organic bases (60).

Methyl red has been used in place of methyl orange in titrations in "G-H" solvent (54), and, in solvents such as ethylene glycol, for the determination of calcium oxide and hydroxide in lime and silicate products (61). Acetone has been used as the solvent in the assay of pharmaceutical products containing promazine and chlorpromazine (members of the phenothiazine type of antihistamines and tranquillizing drugs) (62). Acetic acid in acetic anhydride has been titrated with triethylamine in benzene solution (63). A

rapid control determination for amines in hydrocarbon-polymerization feeds involves back-titration of perchloric acid with a solution of diphenylguanidine in diethyl Cello-solve (64). In most of the above determinations, the indicator was added as a 0.1 per cent solution in glacial acetic acid.

Methyl Yellow (dimethyl yellow); *p*-dimethylaminoazobenzene (C.I. 11020), was used in the first recorded nonaqueous titration in benzene (29). Thirty years later, Vorländer and his co-workers (65, 66) investigated some of the analytical possibilities of nonaqueous titrimetry. They showed that many amines, including certain alkaloids, could be titrated in chloroform solution. In these studies, the indicator was made up in chloroform solution. Further studies have been made with *p*-toluenesulfonic acid in chloroform as a titrant and with the color change of the indicator sharpened by addition of phenol, which also improves the solvent power of the medium (67). This sulfonic acid has been used as titrant in the assay of atropine, lobeline, and harmine (68) and in the determination of diacidic bases like nicotine in mixtures with monoacidic bases (69, 70).

Vorländer's method has been adapted to the micro scale, so that a sample containing 0.5 to 3.0 mg. of an alkaloid base may be satisfactorily titrated in chloroform (71). This method has been used for the titrimetric study of the effectiveness of separation of atropine from its breakdown products (72), the titration of tomatine and tomatidine (73), and the estimation of ergot alkaloids (74).

Methyl yellow screened with methylene blue has been used as an indicator for the titration of chrysanthemum monocarboxylic acid in commercial allethrin (75). The solvent is methanol; and the titrant, methanolic potassium hydroxide. The same mixed indicator and solvent have been employed for the determination of chrysanthemum monocarboxylic anhydride by the addition of an excess of morpholine and back-titration with methanolic hydrochloric acid. The latter method has also served for the assessment of the purity of various other carboxylic acid anhydrides (76). For the determination of hydrochloric and sulfuric acids in their mixtures, the morpholine titration in acetonitrile

solution gives an end point when all the hydrochloric acid and one-half of the sulfuric acid have been titrated (77). As part of the extensive studies on acid-base equilibria in glacial acetic acid, the ionization and dissociation constants of methyl yellow in this solvent have been determined (78).

Miscellaneous Azo Indicators. For the titration of phenols in ethylenediamine medium, *p*-nitro-*p*'-aminoazobenzene (C.I. 11005) was found to be suitable (44). Certain 4-hydroxycoumarin derivatives have been titrated in pyridine with ethanolic potassium hydroxide, the indicator being a solution of 4-(*p*-nitrophenylazo)pyrocatechol (79). Carboxylic acids in the presence of phenols have been titrated in acetone with potassium methoxide, *p*-hydroxyazobenzene (C.I. 11800) being the indicator (34). Alcohols and phenols dissolved in tetrahydrofuran have been determined by interaction with lithium aluminum hydride and back-titration with a standard solution of alcohol using *p*-phenylamino-azobenzene as indicator (80).

Tropaeolin 00 (orange IV), sodium *p*-diphenylamino-azobenzenesulfonate, (C.I. 13080) has been used in the perchloric acid titration of alkaloids and of certain pharmaceutically important sodium salts dissolved in acetic acid (81). Aminopyrine dissolved in benzene-acetic acid has been titrated with perchloric acid dissolved in acetic acid (82). *Tropaeolin 00* has been employed in the differential titration of mixtures containing caffeine, sodium salicylate, etc. (83). *Congo red*, disodium diphenyl-*bis*-(azo-naphthionate) (C.I. 22120), has been used as the second stage indicator in the analysis of aliphatic primary and secondary plus tertiary amines (84). The same indicator was one of the several which proved successful for acid-base titrations in dioxan and other solvents containing 10 per cent water (85). *Congo red* was one of the numerous indicators which were tried and proved unsuitable for titrimetry in anhydrous sulfuric acid (86). Various azo compounds have been used for the titrimetric study of Lewis acids (87), of the acidity of catalyst surfaces (88), and in the determination of very weak acids by reaction with lithium aluminum hydride (89).

Triphenylmethane Compounds

Triphenylmethane compounds have received the greatest attention in nonaqueous acid-base titrimetry, particularly in glacial acetic acid solvent. Crystal violet and methyl violet are the best known indicators of this group.

Crystal Violet (gentian violet), hexamethyl-*p*-rosaniline chloride (usually admixed with some of the corresponding penta- and tetramethyl compounds (C.I. 42555), has been used more extensively than any other indicator for nonaqueous acid-base titrimetry. The usual solvent is glacial acetic acid, either alone or mixed with acetic anhydride, chloro-

form, etc. Acid-base phenomena in acetic anhydride have been studied (90). Usually perchloric acid in acetic acid or occasionally in another solvent serves as the titrant.

Some materials determined by titrations in acetic acid (unless otherwise qualified) with perchloric acid as titrant and crystal violet as indicator include acetic anhydride in mixtures with acetic acid (addition of aniline and back-titration) (91), alkaloids and their salts (92, 93), tobacco alkaloids (benzene-chloroform solvent) (94), volatile amines in choline salts (95), amino acids (96-99), a wide variety of cadmium halide complexes with aminopyrine, antipyrine, brucine, etc. (acetic acid-dioxan solvent) (100), amphetamine salts (101), local anesthetics (102, 103) and 2-benzhydryloxyimidazoline hydrochloride (Antadril) (104). Further determinations include the titration of antihistamine drugs (105), synthetic antihistamines and pharmaceutically important alkaloids like belladonna (titrant, perchloric acid dissolved in acetic anhydride) (106, 107), diphenhydramine (acetic acid-chloroform solvent) (108), antipyrine derivatives (acetic acid-dioxan solvent) (109), apomorphine hydrochloride (110), barbiturates (111), choline salts of carboxylic acids (112), cocaine hydrochloride and hydrochlorides of other weak bases (113), ephedrine in nasal sprays (chloroform solvent) (114), ergotamine salts (115, 116), and ergotamine phosphate (45).

Fatty amine products (117), isolysergic acid hydrazide (118), isonicotinic hydrazide (acetic acid-chloroform solvent (119)) (120), aminopyrine, antihistaminics, mephedine (Demerol), and similar drugs in suppositories (121), morphine and derivatives (122), inorganic nitrates in explosives (41), quinine bases (123), phenazone (124), picrates of dialkyl sulfides (125) and of 4-mercaptopyridine derivatives (126), purine bases (127) (acetic acid-nitrobenzene solvent (128)), and pyridinecarboxylic acids (129) have been successfully titrated. Finally, reserpine (32), saccharin sodium (111, 130), inorganic chloride, bromide and iodide salts (131), alkali metal salts of citric, salicylic, acetic, benzoic, and tartaric acids (132), salts of amines, basic heterocyclic nitrogen compounds, and quaternary ammonium compounds (133), saponified phthalate esters (134), *S*-alkylthiuronium picrates (135), *S*-benzylthiuronium salts of carboxylic acids (136), sulfonamides (137), thiamine salts (acetic acid-benzene solvent) (138), cocaine and other tropane alkaloids (139), tubocurarine chloride and other alkaloidal halides (140), and xanthates of alcohols (141) have been titrated successfully.

In an extensive study of the behavior of crystal violet as an acid-base indicator in acetic acid, it has been observed that the correct end point color depends upon the system being titrated and should be determined by reference to a potentiometric end point (142). In an investigation of the possible applications and limitations of titrations in

acetic acid, over 400 compounds (including salts of strong bases and weak acids, salts of weak bases and weak acids, and organic bases) have been tested, some by both potentiometric and crystal violet methods (143). In numerous potentiometric and indicator titrations, conducted in acetic acid for the purpose of establishing a *pH* scale in this solvent, crystal violet has been found to be one of the most suitable indicators (144). For the determination of weak organic bases in acrylonitrile, acetic acid has been used as the diluent before titration with perchloric acid (145).

An indirect method for the determination of potassium involves its precipitation with sodium tetraphenylboron. The precipitate is dissolved in a mixture of acetone and acetic acid and titrated hot with perchloric acid (146). The direct determination of oxirane oxygen in epoxy resins, etc., has been accomplished by dissolution of an epoxy compound in chlorobenzene or benzene and titration with a solution of hydrogen bromide in acetic acid (147). In this determination, hydrogen bromide adds rapidly to the oxirane function. The sulfates of streptomycin have been determined in ethylene glycol-acetic acid medium by an indirect titration with potassium biphthalate (148). Crystal violet has been shown to behave reversibly in acetyl chloride medium (149). Propionic acid has been demonstrated to be better than acetic or formic acids in the titration of diphenhydramine (150). Aprotic acids, such as stannic chloride, have been titrated with pyridine in thionyl chloride (151).

The solubility of crystal violet in water and in a variety of mixtures of water with ethanol and other hydroxylic solvents has been determined (152). The interaction of crystal violet base with acids in various organic solvents has also been studied (153).

Methyl Violet, pentamethyl-*p*-rosaniline chloride (usually admixed with varying amounts of the tetra- and hexamethyl compounds) (C.I. 42535) differs from crystal violet only in the extent of methyl substitution; hence, it would be expected to be applicable in similar titrations and in the same solvents. This is borne out in practice; in nearly all cases, acetic acid has been used

as the solvent for the substance to be determined, for the perchloric acid which is nearly always used as the titrant, and very often for the preparation of the indicator solution. Benzene and chlorobenzene are sometimes used for the latter purpose.

Titration in acetic acid with perchloric acid as titrant and methyl violet as indicator have been used for the determination of amines on the micro scale (154), aminotriazole derivatives (38), antipyrine derivatives (109), barbiturates (111), basic nitrogen in benzene (one-tenth to one-quarter the sample volume of glacial acetic acid added prior to titration) (155), organic bases (156), basic nitrogen compounds in petroleum (157), benzocaine (158), and glycine in elixir (159). Further determinations include the titration of hydrazides of pyridinecarboxylic acids, including nicotinic and isonicotinic acids (160), alkali halide (161), nitrate, nitrite, and sulfate salts (162), narcotic drugs and alkaloids (163), papaverine and other nitrogen bases (81), pharmaceutically important amine and alkaloid hydrochlorides (164), and phenazone (124). Picrates of amines (165, 166), pyrazolone in two-component medical preparations (167), pyridinecarboxylic acids (129, 168), alkali salts of organic acids (by addition of excess perchloric acid and back-titration with sodium acetate in acetic acid) (81, 169), Schiff bases (170), saccharin sodium (111), sulfates of organic bases (171), and theobromine and sodium salicylate (172) have been successfully titrated.

Oxirane oxygen has been determined by addition of standard hydrochloric acid in carbon tetrachloride—isopropyl ether, followed by back-titration of the excess of acid not less than six hours later with sodium acetate dissolved in acetic acid (173). Water in acetic acid has been determined by the acid-catalyzed reaction between water and added acetic anhydride. Aniline was then added; after brief standing, the excess was titrated with perchloric acid in acetic acid (174).

The behavior of the tetraphenylboron ion in anhydrous acetic acid has been studied (175). After precipitation with sodium tetraphenylboron, alkaloids and other organic bases have been titrated with perchloric acid after the residue has been dried and dissolved in acetic acid (176). Many nitrogen heterocyclic bases and aliphatic amines have been titrated in dioxan with perchloric acid using methyl violet as indicator (177). The latter, screened with bromophenol blue, has been used in the titration of 5-acetamido-methyl-4-amino-2-methylpyrimidine (178). A mixture of methyl violet and eosin Y, 2',4',5',7'-tetrabromofluo-

rescein (C.I. 45380), has been employed for the "differentiating" titration of amines in dioxan (179). The purification of this solvent for use in nonaqueous titrimetry has been described (180).

Malachite Green, tetramethyl-di-*p*-diaminofuchsonium chloride (C.I. 42000), has been studied as indicator in the perchloric acid titration of a number of alkaloids in acetic acid medium (109, 111, 129). The same solvent and titrant have been used for the determination of phenazone (124), of quinine bases (123), and of xanthenes (181). The latter titration is of interest in that it was followed spectrophotometrically. Malachite green has been employed in a study of the reaction between mercuric acetate and potassium halides in acetic acid (182). A solvent consisting mainly of benzene with a little chloroform has been proved satisfactory for the titration of caffeine (183). Aprotic acids, such as stannic chloride, have been titrated with pyridine in thionyl chloride (151). Titrations in 98 to 98.8 per cent formic acid using malachite green or various other indicators have been studied (184).

Victoria Blue R, a diphenylnaphthylmethane dye (C.I. 44040), has been found suitable for the perchloric acid titration of diethylamine in the presence of large amounts of monoethylamine. A preliminary treatment with acetic anhydride was used to convert the monocompound to the neutral amide so that the unaffected secondary amine might be titrated (98).

(To be continued in June 1959 issue)

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